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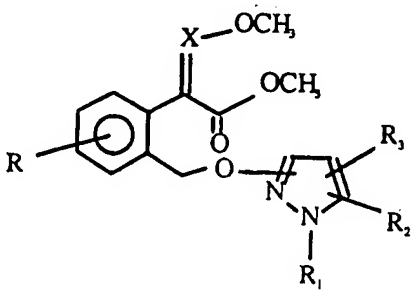

(I)

(57) Abstract

The present invention relates to novel propenoic ester derivatives having pyrazole group of general formula (I) which have active fungicidal properties, wherein R is hydrogen, one or more halogen atoms selected from the group consisting of fluorine and chlorine, methyl, lower alkyl, alkoxy, nitro or phenyl group; R_1 is methyl, lower alkyl, alkenyl, alkynyl, benzyl, aryl, phenyl, substituted phenyl or pyridyl group; R_2 and R_3, as equivalent or different group respectively, are hydrogen, halogen atoms, trifluoromethyl or haloalkyl group; and X is carbon or nitrogen atom.

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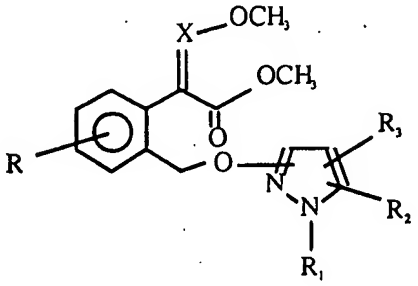
PROPENOIC ESTER DERIVATIVES HAVING PYRAZOLE GROUP AND THE USE

BACKGROUND OF THE INVENTION

Technical Field

The present invention relates to novel propenoic ester derivatives having pyrazole group of the following general formula(I) which have active fungicidal properties.



(I)

wherein,

R is hydrogen, one or more halogen atoms selected from the group consisting of fluorine and chlorine, methyl, lower alkyl, alkoxy, nitro or phenyl group ;

R_1 is methyl, lower alkyl, alkenyl, alkynyl, benzyl, aryl, phenyl, substituted phenyl or pyridyl group ;

R_2 and R_3, as equivalent or different group respectively, are hydrogen, halogen atoms, trifluoromethyl or haloalkyl group ; and

X is carbon or nitrogen atom.

The term "lower alkyl group" referred above designates straight or branch chained alkyl and have from 1 to 6 carbon atoms.

Description of the Prior Art

Even though the known fungicides possess excellent fungicidal properties the development of compounds based upon similar basic structure has given rise to the problem of resistance development by the target fungi due to long exposure to these

compounds with common basic structure.

As a result of continuous effort to solve this problem a novel series of propenoic ester derivative was disclosed firstly in European Patent No. 472300 of ICI Co., U.S.Patent No. 4994495, European Patent No. 422597 of BASF Co., U.S.Patent No. 5003101 and European Patent No. 460575 of Ciba-Geigy Co., but fungicidal activity of the reported compounds was too low thus and offered limited application prior to more improvements.

Therefore, with consideration as to the aforesaid points the present inventors have made effort to develope new fungicidal compounds which have powerful fungicidal activities to various target fungi and low toxicity.

As the result, the inventors of the present invention synthesized novel propenoic ester derivatives by using pyrazole compound which have not been so far known.

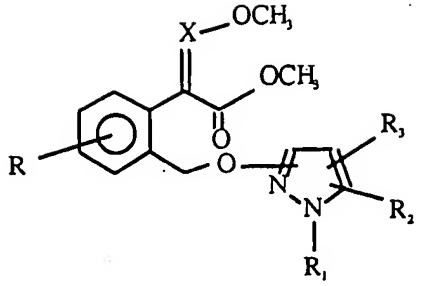
SUMMARY OF THE INVENTION

The objective of the present invention is to provide novel propenoic ester derivatives with strong fungicidal activities toward various fungi and broad fungicidal spectrum and a simple manufacturing process.

Another objective is to provide fungicidal compositions containing said derivatives as active compounds.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is identified as propenoic ester derivatives having pyrazole group which correspond to the following formula(I), and agricultural preparations containing compounds of formula(I) as active ingredient.

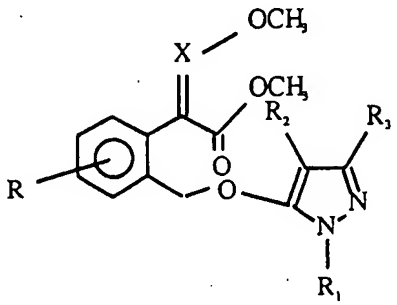


(I)

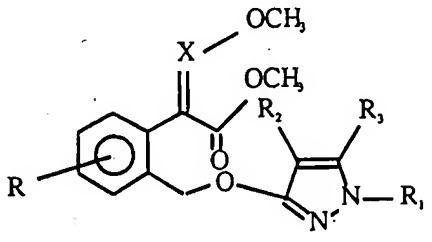
wherein, R, R_1, R_2, R_3 and X are respectively defined as the above.

In the formula(I) according to the present invention the preferred derivatives with greatest fungicidal activities are where R is hydrogen or chlorine, R_1 is methyl or lower alkyl group, R_2 and R_3 are of same or different from either hydrogen atom and trifluoromethyl group

Propenoic ester derivatives of the present invention may be divided to the following formula(I-a) and (I-b) according to the position of substituents introduced in pyrazole group.



(I - a)



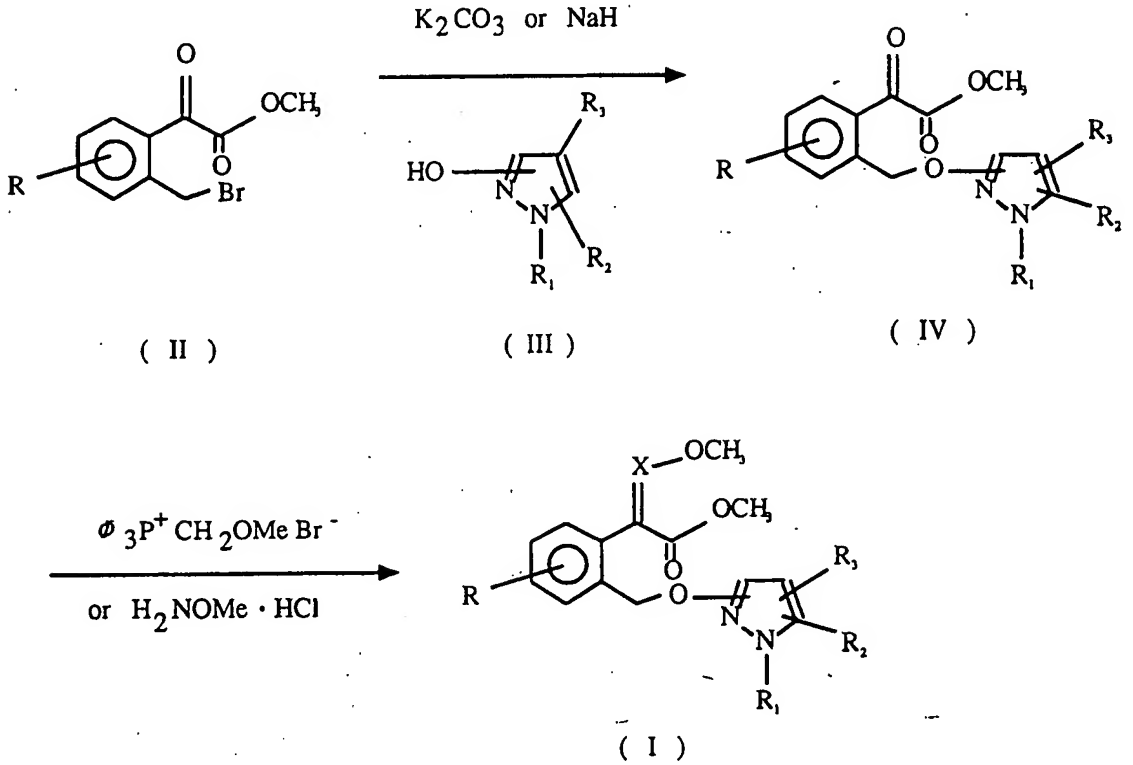
(I - b)

In the above formula(I-a) and (I-b), R, R_1, R_2, R_3 and X are respectively defined as the above.

According to the present invention, propenoic ester derivatives of the above formula(I) can be prepared by reacting the substituted 2-methyloxalylbenzyl bromide of following formula(II) with the pyrazole compound of following formula(III) in the presence of potassium carbonate or sodium hydride to prepare glyoxylate derivatives of the following formula(IV) as intermediate compound and reacting the glyoxylate

derivatives with methoxyl amine or methoxymethyltriphenylphosphine to give compounds of formula(I).

This reaction scheme is as following :



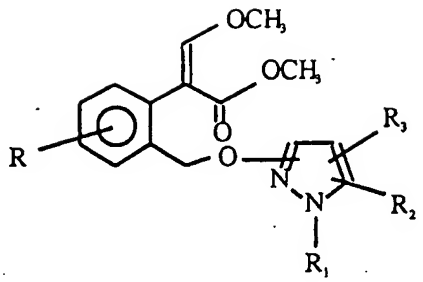
In the above scheme, R, R_1, R_2, R_3 and X are respectively defined.

In the above reaction, the compound of formula (II) is reacted with the same mole of the compound of formula (III) in the presence of potassium carbonate and sodium hydride of each 1~3 equivalence to obtain the compound of formula (IV).

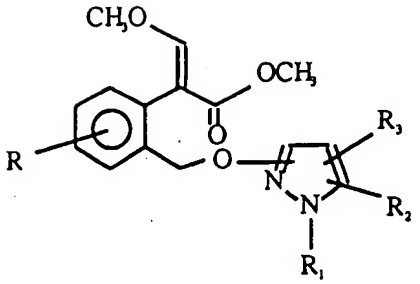
The resulted compound of formula (IV) as an intermediate is reacted with methoxymethyltriphenylphosphine in an organic solvent such as tetrahydrofuran or diethyl ether, or with methoxylamine in an organic solvent such as dichloromethane, 1, 2-dichloroethane, ethanol, etc., to obtain the desired compound of formula (I).

The completion of aforesaid reaction is realized when the compound of formula (IV) remains no more in the reaction. It can be easily checked by T. L. C.

According to the present invention, the obtained compound (I) consists of steroisomers (cis- and trans- form) of the following structural formulas.



cis - form

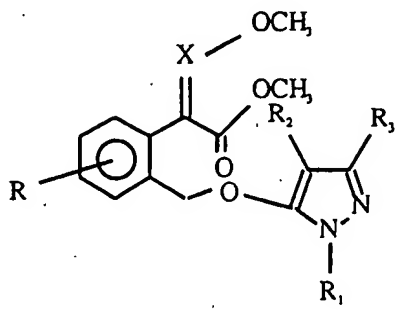


trans - form

The fungicidal activies of the compound(I) according to the present invention were tested for mixture of isomers as well as individual isolated isomer when isolation was possible.

New propenoic ester derivatives of formula (I) ,which are divided to formula (Ia) and (Ib), are typically listed in the following Table 1 and 2.

Table 1.



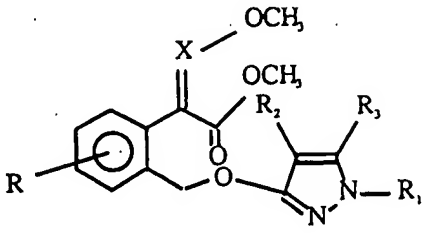
(I - a)

Comp. No.	R	R_1	R_2	R_3	X
1	H	CH_3	H	CF_3	cis-CH
2	H	CH_3	H	CF_3	trans-CH
3	H	CH_3	H	CF_3	cis-N
4	H	CH_3	H	CF_3	trans-N
5	H	CH_3	H	Cl	-CH
6	H	CH_3	H	CHF_2	-CH
7	H	CH_3	H	H	-CH

Comp. No.	R	R_1	R_2	R_3	X
8	H	CH_3	H	CH_3	-CH
9	H	CH_3	Br	CF_3	-CH
10	H	CH_3	Cl	CF_3	-CH
11	H	CH_3	CO_2Et	H	-CH
12	H	CH_3	CO_2Et	H	-N
13	H	C_2H_5	H	CF_3	cis-CH
14	H	C_2H_5	H	CF_3	trans-CH
15	H	C_2H_5	H	CF_3	-N
16	H	i-Pr	H	CF_3	-CH
17	H	i-Pr	H	CF_3	-N
18	H	c-Pr	H	CF_3	-CH
19	H	c-Pr	H	CF_3	-N
20	H	CH_2CF_3	H	CF_3	-CH
21	H	$CH_2CH=CH_2$	H	CF_3	-CH
22	H	$CH_2C\equiv CH$	H	CF_3	-CH
23	H	n-Bu	H	CF_3	-CH
24	H	i-Bu	H	CF_3	-CH
25	H	phenyl	H	CF_3	-CH
26	H	phenyl	H	CF_3	cis-CH
27	H	phenyl	H	CF_3	trans-CH
28	H	2-pyridyl	H	CF_3	-N
29	H	3-fluorophenyl	H	CF_3	-CH
30	H	3-chlorophenyl	H	CF_3	-CH
31	4-Cl	CH_3	H	CF_3	-CH
32	4-Cl	CH_3	H	CF_3	-N

Comp. No.	R	R_1	R_2	R_3	X
33	4-Cl	C_2H_5	H	CF_3	-CH
34	3-Cl	CH_3	H	CF_3	-CH
35	3,4-Cl_2	CH_3	H	CF_3	-CH
36	3-NO_2	CH_3	H	CF_3	-CH
37	3-NO_2	CH_3	H	CF_3	-CH
38	3-CH_3	CH_3	H	CF_3	-CH
39	4-CH_3	CH_3	H	CF_3	-CH
40	3-CH_3O	CH_3	H	CF_3	-CH
41	4-CH_3O	CH_3	H	CF_3	-CH
42	4-C_2H_5	CH_3	H	CF_3	-CH
43	4,5 — 	CH_3	H	CF_3	-CH

Table 2.



(I - b)

Comp. No.	R	R_1	R_2	R_3	X
44	H	CH_3	H	CF_3	cis-CH
45	H	CH_3	H	CF_3	trans-CH
46	H	CH_3	H	CF_3	cis-N
47	H	CH_3	H	CF_3	trans-N

Comp. No.	R	R_1	R_2	R_3	X
48	H	CH_3	H	Cl	CH
49	H	CH_3	H	CH_3	CH
50	H	CH_3	H	H	CH
51	H	CH_3	Cl	CF_3	CH
52	H	C_2H_5	H	CF_3	CH
53	H	C_2H_5	H	CF_3	CH
54	H	i-Pr	H	CF_3	CH
55	H	i-Pr	H	CH_3	N
56	H	c-Pr	H	CF_3	CH
57	H	c-Pr	H	CF_3	N
58	4-Cl	CH_3	H	CF_3	CH
59	4-Cl	CH_3	H	CF_3	CH
60	4-Cl	C_2H_5	H	CF_3	CH
61	4-Cl	C_2H_5	H	CF_3	N
62	3-Cl	CH_3	H	CF_3	CH
63	3,4-Cl_2	CH_3	H	CF_3	CH
64	3-NO_2	CH_3	H	CF_3	CH
65	4-NO_2	CH_3	H	CF_3	CH
66	4-CH_3	CH_3	H	CF_3	CH
67	3-CH_3O	CH_3	H	CF_3	CH
68	4-C_2H_5	CH_3	H	CF_3	CH
69	4,5 – 	CH_3	H	CF_3	CH

EXAMPLE 1

cis-Methyl-2-[2-(1-methyl-3-trifluoromethyl-5-pyrazoyl)-methyl-phenyl]-3-methoxy propenoate(Comp. No. 1)

trans-Methyl-2-[2-(1-methyl-3-trifluoromethyl-5-pyrazoyl)-methyl-phenyl]-3-methoxy propenoate (Comp. No. 2)

To a solution of methoxymethyltriphenylphosphonium chloride (298mg, 0.87 mmol) in tetrahydrofuran at -78℃ was added dropwise sec-butyllithium (1.3M in cyclohexane, 740μl, 0.95 mmol). After stirring at -78℃ for 1hr, a solution of methyl-2-[2-(1-methyl-3-trifluoromethyl-5-pyrazoyl)-methyl-phenyl]glyoxylate (268mg, 0.78mmol) in tetrahydrofuran(1 ml) was added dropwise over 10 minutes at -78℃ to the reaction mixture. The reaction was allowed to proceed for 6hr at -78℃, and then quenched by addition of diethyl ether(30ml) and water(10ml). The aqueous layer was extracted with diethyl ether. The combined organic extracts were washed with brine, dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure to afford crude product. Final purification was effected by silica-gel column chromatography(ethyl acetate-hexane, 1 : 3) to afford the compound No. 1 of cis-isomer(110mg, yield = 33%, Rf=0.25) and the compound No. 2 of trans-isomer(130mg, yield=41%, Rf=0.35).

Comp. No. 1

^{1}H NMR($CDCl_3$): δ 3.82(brs, 6H), 3.95(s, 3H), 5.10(s, 2H), 5.85(s, 1H), 6.75(s, 1H), 7.25-7.60(m, 4H)

m/e : 370(M^+)

Comp. No. 2

^{1}H NMR($CDCl_3$): δ 3.82(brs, 6H), 3.90(s, 3H), 5.05(s, 2H), 5.85(s, 1H), 7.05-7.80(m, 4H), 7.60(s, 1H)

m/e : 370(M^+)

EXAMPLE 2

cis-Methyl-2-[2-(1-methyl-3-trifluoromethyl-5-pyrazoyl)-methyl-

phenyl]glyoxylate methyloxime (Comp. No. 3)

trans-Methyl-2-[2-(1-methyl-3-trifluoromethyl-5-pyrazoyl)-methyl-phenyl]glyoxylate methyloxime (Comp. No. 4)

To a solution of methyl-2-[2-(1-methyl-3-trifluoromethyl-5-pyrazoyl)-methyl-phenyl]glyoxylate (250mg, 0.73 mmole) in methanol(5 ml) at room temperature was added methoxylamine hydrochloride(250mg, 3mmol) and pyridine(600 μl, 7.3 mmol), and then heated to 70℃. After being stirred at 70℃ for 12hr, the reaction mixture was concentrated under reduced pressure, diluted with dichloromethane(15 ml) and water(10 ml). The aqueous layer was extracted with dichloromethane. The combined organic extrats were washed with brine, dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure to afford crude product. Final purification was effected by silica-gel column chlormatography(ethyl acetate-hexane, 1 : 3) to afford the compound No. 3 of cis-isomer(75mg, yield = 28%, Rf=0.3) and the compound No. 4 of trans-isomer(95mg, yield=36%, Rf=0.4).

Comp. No. 3

^{1}H NMR($CDCl_3$): δ 3.75(s, 3H), 3.85(s, 3H), 3.95(s, 3H), 4.95(s, 2H)
5.85(s, 1H), 7.05-7.40(m, 4H)

m/e : 371(M^+)

Comp. No. 4

^{1}H NMR($CDCl_3$): δ 3.70(s, 3H), 3.85(s, 3H), 3.92(s, 3H), 5.35(s, 2H)
5.80(s, 1H), 7.40-7.65(m, 4H)

m/e : 371(M^+)

EXAMPLE 3

Methyl-2-[2-(1-methyl-5-pyrazoyl)-methyl-phenyl]-3-methoxypropenoate (Comp. No. 7)

To a solution of methoxymethyltriphenylphosphonium chloride (88mg, 0.26 mmol) in tetrahydrofuran at -78℃ was added dropwise sec-butyllithium (1.3M in cyclohexane, 214 μl, 0.28 mmol). After stirring at -78℃ for 1hr, a solution of

methyl-2-[2-(1-methyl-5-pyrazoyl)-methyl-phenyl]glyoxylate (70mg, 0.25mmol) in tetrahydrofuran(1 *ml*) was added dropwise over 10 minutes at -78℃ to the reaction mixture. The reaction was allowed to proceed for 6hr at -78℃, and then quenched by addition of diethyl ether(30*ml*) and water(10*ml*). The aqueous layer was extracted with diethyl ether. The combined organic extracts were washed with brine, dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure to afford crude product. Final purification was effected by silica-gel column chromatography(ethyl acetate-hexane, 1 : 2) to afford the compound No. 7 (60mg, yield = 81%).

^{1}H NMR($CDCl_3$): δ 3.80(brs, 6H), 3.85(s, 3H), 5.10(s, 2H), 6.80(s, 1H), 7.05-7.80(m, 4H), 7.45(s, 1H), 7.60(s, 1H)

m/e : 302(M^+)

EXAMPLE 4

Methyl-2-[2-(1,3-dimethyl-5-pyrazoyl)-methyl-phenyl]-3-methoxypropenoate (Comp. No. 8)

To a solution of methoxymethyltriphenylphosphonium chloride (180mg, 0.52 mmol) in tetrahydrofuran at -78℃ was added dropwise sec-butyllithium (1.3M in cyclohexane, 440μl, 0.56 mmol). After stirring at -78℃ for 1hr, a solution of methyl-2-[2-(1,3-dimethyl-5-pyrazoyl)-methyl-phenyl]glyoxylate (120mg, 0.5mmol) in tetrahydrofuran(1 *ml*) was added dropwise over 10 minutes at -78℃ to the reaction mixture. The reaction was allowed to proceed for 6hr at -78℃, and then quenched by addition of diethyl ether(30*ml*) and water(10*ml*). The aqueous layer was extracted with diethyl ether. The combined organic extracts were washed with brine, dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure to afford crude product. Final purification was effected by silica-gel column chromatography(ethyl acetate-hexane, 1 : 2) to afford the compound No. 8(100mg, yield = 77%).

^{1}H NMR($CDCl_3$): δ 2.19(s, 3H), 3.60(s, 3H), 3.71(s, 3H), 3.85(s, 3H),

4.97(s, 2H), 5.29(s, 1H), 7.35-7.75(m, 5H)

m/e : 316(M^+)

EXAMPLE 5

Methyl-2-[2-(4-bromo-1-methyl-3-trifluoromethyl-5-pyrazoyl)-methyl-phenyl]-3-methoxypropenoate (Comp. No. 9)

To a solution of methoxymethyltriphenylphosphonium chloride (402mg, 1.18 mmol) in tetrahydrofuran at -78℃ was added dropwise sec-butyllithium (1.3M in cyclohexane, 950μl, 1.23 mmol). After stirring at -78℃ for 1hr, a solution of methyl-2-[2-(4-bromo-1-methyl-3-trifluoromethyl-5-pyrazoyl)-methyl-phenyl]glyoxylate (450mg, 1.07mmol) in tetrahydrofuran(1 ml) was added dropwise over 10 minutes at -78℃ to the reaction mixture. The reaction was allowed to proceed for 6hr at -78℃, and then quenched by addition of diethyl ether(30ml) and water(10ml). The aqueous layer was extracted with diethyl ether. The combined organic extracts were washed with brine, dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure to afford crude product. Final purification was effected by silica-gel column chromatography(ethyl acetate-hexane, 1 : 3) to afford the compound No. 9 (250mg, yield = 56%).

^{1}H NMR($CDCl_3$): δ 3.75(s, 3H), 3.84(s, 3H), 3.98(s, 3H), 5.15(s, 2H),
7.60(s, 1H), 7.15-7.90(m, 4H)

EXAMPLE 6

cis-Methyl-2-[2-(1-ethyl-3-trifluoromethyl-5-pyrazoyl)-methyl-phenyl]-3-methoxypropenoate (Comp. No. 13)

trans-Methyl-2-[2-(1-ethyl-3-trifluoromethyl-5-pyrazoyl)-methyl-phenyl]-3-methoxypropenoate (Comp. No. 14)

To a solution of methoxymethyltriphenylphosphonium chloride (324mg, 0.95 mmol) in tetrahydrofuran at -78℃ was added dropwise sec-butyllithium (1.3M in cyclohexane, 730μl, 0.95 mmol). After stirring at -78℃ for 1hr, a solution of

methyl-2-[2-(1-ethyl-3-trifluoromethyl-5-pyrazoyl)-methyl-phenyl]glyoxylate (260mg, 0.86mmol) in tetrahydrofuran(1 *ml*) was added dropwise over 10 minutes at -78℃ to the reaction mixture. The reaction was allowed to proceed for 6hr at -78℃, and then quenched by addition of diethyl ether(30*ml*) and water(10*ml*). The aqueous layer was extracted with diethyl ether. The combined organic extracts were washed with brine, dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure to afford crude product. Final purification was effected by silica-gel column chromatography(ethyl acetate-hexane, 1 : 2) to afford the compound No. 13 of cis-isomer(70mg, yield = 27%, Rf=0.3) and the compound No. 14 of trans-isomer(100mg, yield=37%, Rf=0.35).

Comp. No. 13

^{1}H NMR($CDCl_3$): δ 1.39(t, 3H), 3.71(s, 3H), 3.89(s, 3H), 4.05(q, 2H), 5.08(s, 2H), 5.74(s, 1H), 6.59(s, 1H), 7.19-7.51(m, 4H)

m/e : 384(M^+)

Comp. No. 14

^{1}H NMR($CDCl_3$): δ 1.40(t, 3H), 3.71(s, 3H), 3.82(s, 3H), 4.05(q, 2H), 5.03(s, 2H), 5.70(s, 1H), 7.20-7.51(m, 4H), 7.61(s, 1H)

m/e : 384(M^+)

EXAMPLE 7

Methyl-2-[2-(1-ethyl-3-trifluoromethyl-5-pyrazoyl)-methyl-phenyl]glyoxylate methyloxime (Comp. No. 15)

To a solution of methyl-2-[2-(1-ethyl-3-trifluoromethyl-5-pyrazoyl)-methyl-phenyl]glyoxylate (70mg, 0.2 mmole) in methanol(5*ml*) at room temperature was added methoxylamine hydrochloride(80mg, 1mmol) and pyridine(250μl, 3 mmol), and then heated to 70℃. After being stirred at 70℃ for 12hr, the reaction mixture was concentrated under reduced pressure, diluted with dichloromethane(15*ml*) and water(10 *ml*). The aqueous layer was extracted with dichloromethane. The combined organic extrats were washed with brine, dried over anhydrous magnesium sulfate,

filtered, and concentrated under reduced pressure to afford crude product. Final purification was effected by silica-gel column chlomatography(ethyl acetate-hexane, 1 : 5) to afford the compound No. 15 (70mg, yield = 91%).

^{1}H NMR($CDCl_3$): δ 3.37(t, 3H), 3.85(s, 3H), 4.03(s, 3H), 4.11(q, 2H), 5.00(s, 2H), 5.71(s, 1H), 7.20-7.51(m, 4H)

m/e : 385(M^+)

EXAMPLE 8

Methyl-2-{2-[1-(2',2',2'-trifluoroethyl)-3-trifluoromethyl-5-pyrazoyl]-methyl-phenyl}-3-methoxypropenoate (Comp. No. 20)

To a solution of methoxymethyltriphenylphosphonium chloride (460mg, 1.34 mmol) in tetrahydrofuran at -78℃ was added dropwise sec-butyllithium (1.3M in cyclohexane, 1.2μl, 1.46 mmol). After stirring at -78℃ for 1hr, a solution of methyl-2-{2-[1-(2',2',2'-trifluoroethyl)-3-trifluoromethyl-5-pyrazoyl]-methyl-phenyl}glyoxylate (500mg, 1.22mmol) in tetrahydrofuran(1 ml) was added dropwise over 10 minutes at -78℃ to the reaction mixture. The reaction was allowed to proceed for 6hr at -78℃, and then quenched by addition of diethyl ether(30ml) and water(10ml). The aqueous layer was extracted with diethyl ether. The combined organic extracts were washed with brine, dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure to afford crude product. Final purification was effected by silica-gel column chromatography(ethyl acetate-hexane, 1 : 3) to afford the compound No. 20 (270mg, yield = 53%).

^{1}H NMR($CDCl_3$): δ 3.70(s, 3H), 3.80(s, 3H), 4.30-4.70(m, 2H), 5.10(s, 2H), 5.80(s, 1H), 7.10-7.60(m, 4H), 7.55(s, 1H)

EXAMPLE 9

Methyl-2-[2-(1-allyl-3-trifluoromethyl-5-pyrazoyl)-methyl-phenyl]-3-methoxypropenoate (Comp. No. 21)

To a solution of methoxymethyltriphenylphosphonium chloride (205mg, 0.6

mmol) in tetrahydrofuran at -78℃ was added dropwise sec-butyllithium (1.3M in cyclohexane, 500㎕, 0.65 mmol). After stirring at -78℃ for 1hr, a solution of methyl-2-[2-(1-allyl-3-trifluoromethyl-5-pyrazoyl)-methyl-phenyl]glyoxylate (200mg, 0.54mmol) in tetrahydrofuran(1 *ml*) was added dropwise over 10 minutes at -78℃ to the reaction mixture. The reaction was allowed to proceed for 6hr at -78℃, and then quenched by addition of diethyl ether(30*ml*) and water(10*ml*). The aqueous layer was extracted with diethyl ether. The combined organic extracts were washed with brine, dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure to afford crude product. Final purification was effected by silica-gel column chromatography(ethyl acetate-hexane, 1 : 3) to afford the compound No. 21 (115mg, yield = 56%).

^{1}H NMR($CDCl_3$): δ 3.70(s, 3H), 3.85(s, 3H), 4.70(d, 2H), 5.10(s, 2H)
5.05-6.00(m, 4H), 7.15-7.70(m, 4H), 7.50(s, 1H)

m/e : 396(M^+)

EXAMPLE 10

Methyl-2-[2-(1-propargyl-3-trifluoromethyl-5-pyrazoyl)-methyl-phenyl]-3-methoxypropenoate (Comp. No. 22)

To a solution of methoxymethyltriphenylphosphonium chloride (160mg, 0.45 mmol) in tetrahydrofuran at -78℃ was added dropwise sec-butyllithium (1.3M in cyclohexane, 420㎕, 0.51 mmol). After stirring at -78℃ for 1hr, a solution of methyl-2-[2-(1-propargyl-3-trifluoromethyl-5-pyrazoyl)-methyl-phenyl]glyoxylate (150mg, 0.42mmol) in tetrahydrofuran(1 *ml*) was added dropwise over 10 minutes at -78℃ to the reaction mixture. The reaction was allowed to proceed for 6hr at -78℃, and then quenched by addition of diethyl ether(30*ml*) and water(10*ml*). The aqueous layer was extracted with diethyl ether. The combined organic extracts were washed with brine, dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure to afford crude product. Final purification was effected by silica-gel column chromatography(ethyl acetate-hexane, 1 : 3) to afford the compound

No. 22 (103mg, yield = 66%).

^{1}H NMR($CDCl_3$): δ 1.90(t, 3H), 3.35(d, 3H), 3.65(s, 3H), 3.78(s, 3H), 5.06(s, 2H), 7.10-7.80(m, 4H), 7.55(s, 1H)

EXAMPLE 11

trans-Methyl-2-[2-(1-phenyl-3-trifluoromethyl-5-pyrazoyl)-methyl-phenyl]-3-methoxypropenoate (Comp. No. 26)

To a solution of methoxymethyltriphenylphosphonium chloride (282mg, 0.82 mmol) in tetrahydrofuran at -78℃ was added dropwise sec-butyllithium (1.3M in cyclohexane, 700μl, 0.9 mmol). After stirring at -78℃ for 1hr, a solution of methyl-2-[2-(1-phenyl-3-trifluoromethyl-5-pyrazoyl)-methyl-phenyl]glyoxylate (303mg, 0.75mmol) in tetrahydrofuran(1 ml) was added dropwise over 10 minutes at -78℃ to the reaction mixture. The reaction was allowed to proceed for 6hr at -78℃, and then quenched by addition of diethyl ether(30ml) and water(10ml). The aqueous layer was extracted with diethyl ether. The combined organic extracts were washed with brine, dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure to afford crude product. Final purification was effected by silica-gel column chromatography(ethyl acetate-hexane, 1 : 3) to afford the compound No. 26 (109mg, yield = 35%).

^{1}H NMR($CDCl_3$): δ 3.65(s, 3H), 3.75(s, 3H), 5.12(s, 2H), 5.95(s, 1H), 7.01(s, 1H), 7.20-7.75(m, 9H)

m/e : 462(M^+)

EXAMPLE 12

Methyl-2-[2-(1-phenyl-3-trifluoromethyl-5-pyrazoyl)-methyl-phenyl]glyoxylate methyloxime (Comp. No. 27)

To a solution of methyl-2-[2-(1-phenyl-3-trifluoromethyl-5-pyrazoyl)-methyl-phenyl]glyoxylate (210mg, 0.5 mmole) in methanol(5ml) at room temperature was added methoxylamine hydrochloride(160mg, 2 mmol) and pyridine(405μl, 5 mmol),

and then heated to 70℃. After being stirred at 70℃ for 12hr, the reaction mixture was concentrated under reduced pressure, diluted with dichloromethane(15*ml*) and water(10*ml*). The aqueous layer was extracted with dichloromethane. The combined organic extrats were washed with brine, dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure to afford crude product. Final purification was effected by silica-gel column chlomatography(ethyl acetate-hexane, 1 : 7) to afford the compound No. 27 of cis-isomer(170mg, yield =79%).

^{1}H NMR($CDCl_3$): δ 3.85(s, 3H), 3.95(s, 3H), 5.40(s, 2H), 5.95(s, 1H), 7.30-7.80(m, 9H)

m/e : 463(M^+)

EXAMPLE 13

Methyl-2-[2-(1-pyridyl-3-trifluoromethyl-5-pyrazoyl)-methyl-phenyl]-3-methoxypropenoate (Comp. No. 28)

To a solution of methoxymethyltriphenylphosphonium chloride (216mg, 0.63 mmol) in tetrahydrofuran at -78℃ was added dropwise sec-butyllithium (1.3M in cyclohexane, 500μl, 0.66 mmol). After stirring at -78℃ for 1hr, a solution of methyl-2-[2-(1-pyridyl-3-trifluoromethyl-5-pyrazoyl)-methyl-phenyl]glyoxylate (200mg, 0.57mmol) in tetrahydrofuran(1 *ml*) was added dropwise over 10 minutes at -78℃ to the reaction mixture. The reaction was allowed to proceed for 6hr at -78℃, and then quenched by addition of diethyl ether(30*ml*) and water(10*ml*). The aqueous layer was extracted with diethyl ether. The combined organic extracts were washed with brine, dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure to afford crude product. Final purification was effected by silica-gel column chromatography(ethyl acetate-hexane, 1 : 2) to afford the compound No. 28 (120mg, yield = 58%).

^{1}H NMR($CDCl_3$): δ 3.65(s, 3H), 3.80(s, 3H),5.16(s, 2H), 5.82(s, 1H), 7.20-7.90(m, 7H), 7.57(s, 1H), 8.61(d, 1H)

m/e : 463(M^+)

EXAMPLE 14

Methyl-2-[2-(1-methyl-3-trifluoromethyl-5-pyrazoyl)-methyl-4-chlorophenyl]-3-methoxypropenoate (Comp. No. 31)

To a solution of methoxymethyltriphenylphosphonium chloride (331mg, 0.97 mmol) in tetrahydrofuran at -78℃ was added dropwise sec-butyllithium (1.3M in cyclohexane, 840㎕, 1.1 mmol). After stirring at -78℃ for 1hr, a solution of methyl-2-[2-(1-methyl-3-trifluoromethyl-5-pyrazoyl)-methyl-4-chlorophenyl]glyoxylate (310mg, 0.97mmol) in tetrahydrofuran(1 *ml*) was added dropwise over 10 minutes at -78℃ to the reaction mixture. The reaction was allowed to proceed for 6hr at -78℃, and then quenched by addition of diethyl ether(30*ml*) and water(10*ml*). The aqueous layer was extracted with diethyl ether. The combined organic extracts were washed with brine, dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure to afford crude product. Final purification was effected by silica-gel column chromatography(ethyl acetate-hexane, 1 : 3) to afford the compound No. 31 (160mg, yield = 47%).

^{1}H NMR($CDCl_3$): δ 3.80(brs, 6H), 3.90(s, 3H),5.10(s, 2H), 5.85(s, 1H), 7.05-7.95(m, 3H), 7.65(s, 1H)

EXAMPLE 15

cis-Methyl-2-[2-(1-methyl-5-trifluoromethyl-3-pyrazoyl)-methyl-phenyl]-3-methoxypropenoate (Comp. No. 44)

trans-Methyl-2-[2-(1-methyl-5-trifluoromethyl-3-pyrazoyl)-methyl-phenyl]-3-methoxypropenoate (Comp. No. 45)

To a solution of methoxymethyltriphenylphosphonium chloride (3.28g, 9.6 mmol) in tetrahydrofuran at -78℃ was added dropwise sec-butyllithium (1.3M in cyclohexane, 8*ml* , 10.5 mmol). After stirring at -78℃ for 1hr, a solution of methyl-2-[2-(1-methyl-5-trifluoromethyl-3-pyrazoyl)-methyl-phenyl]glyoxylate (3g, 8.8mmol) in tetrahydrofuran(1 *ml*) was added dropwise over 10 minutes at -78℃ to the reaction mixture. The reaction was allowed to proceed for 6hr at -78℃, and then quenched by

addition of diethyl ether(30*ml*) and water(10*ml*). The aqueous layer was extracted with diethyl ether. The combined organic extracts were washed with brine, dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure to afford crude product. Final purification was effected by silica-gel column chromatography(ethyl acetate-hexane, 1 : 3) to afford the compound No. 44 of cis-isomer(1.1g, yield = 35%, Rf=0.25) and the compound No. 45 of trans-isomer(1.3g, yield=39%, Rf=0.35).

Comp. No. 44

^{1}H NMR($CDCl_3$): δ 3.85(s, 3H), 3.90(s, 3H), 3.96(s,3H), 5.10(s, 2H), 6.01(s, 1H), 6.65(s, 1H), 7.10-7.65(m, 4H)

m/e : 370(M^+)

Comp. No. 45

^{1}H NMR($CDCl_3$): δ 3.85(s, 3H), 3.94(s, 6H), 5.10(s, 2H), 6.05(s, 1H), 7.15-7.55(m, 4H), 7.65(s, 1H)

m/e : 370(M^+)

EXAMPLE 16

Methyl-2-[2-(1-methyl-5-trifluoromethyl-3-pyrazoyl]-methyl-4-chlorophenyl]-3-methoxypropenoate(Comp. No. 58)

To a solution of methoxymethyltriphenylphosphonium chloride (352mg, 1.03 mmol) in tetrahydrofuran at -78℃ was added dropwise sec-butyllithium (1.3M in cyclohexane, 840μl, 1.1mmol). After stirring at -78℃ for 1hr, a solution of methyl-2-[2-(1-methyl-5-trifluoromethyl-3-pyrazoyl)-methyl-4-chlorophenyl]glyoxylate (330mg, 1.03mmol) in tetrahydrofuran(1 *ml*) was added dropwise over 10 minutes at -78℃ to the reaction mixture. The reaction was allowed to proceed for 6hr at -78℃, and then quenched by addition of diethyl ether(30*ml*) and water(10*ml*). The aqueous layer was extracted with diethyl ether. The combined organic extracts were washed with brine, dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure to afford crude product. Final purification was effected by

silica-gel column chromatography(ethyl acetate-hexane, 1 : 3) to afford the compound No. 58 (155mg, yield = 44%).

^{1}H NMR($CDCl_3$): δ 3.85(s, 3H), 3.93(s, 3H), 3.96(s, 3H), 5.13(s, 2H), 6.05(s, 1H), 7.10-7.75(m, 3H), 7.65(s, 1H)

EXAMPLE 17

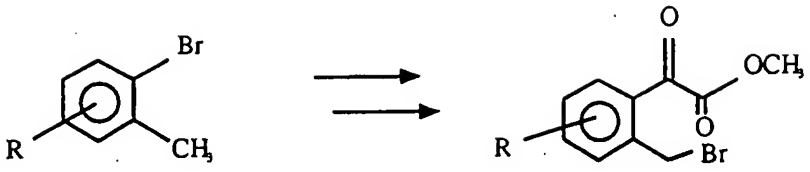
Methyl-2-[3-(1-methyl-5-trifluoromethyl-3-pyrazoyl)-methyl-2-naphthyl]-3-methoxypropenoate (Comp. No. 69)

To a solution of methoxymethyltriphenylphosphonium chloride (190mg, 0.55 mmol) in tetrahydrofuran at -78℃ was added dropwise sec-butyllithium (1.3M in cyclohexane, 460μl, 0.6 mmol). After stirring at -78℃ for 1hr, a solution of methyl-2-[3-(1-methyl-5-trifluoromethyl-3-pyrazoyl)-methyl-2-naphtyl]glyoxylate (190mg, 0.5 mmol) in tetrahydrofuran(1 ml) was added dropwise over 10 minutes at -78℃ to the reaction mixture. The reaction was allowed to proceed for 6hr at -78℃, and then quenched by addition of diethyl ether(30ml) and water(10ml). The aqueous layer was extracted with diethyl ether. The combined organic extracts were washed with brine, dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure to afford crude product. Final purification was effected by silica-gel column chromatography(ethyl acetate-hexane, 1 : 3) to afford the compound No. 69 (115mg, yield = 57%).

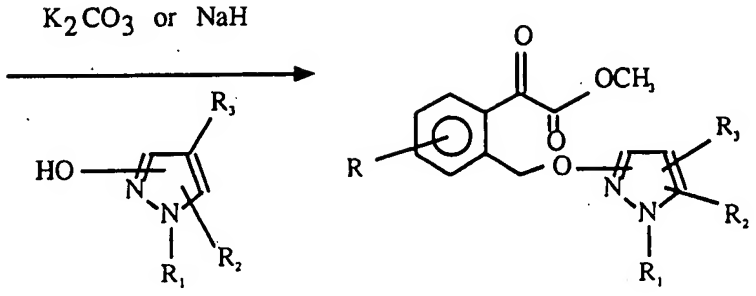
^{1}H NMR($CDCl_3$): δ 3.80(s, 3H), 3.91(s, 3H), 3.95(s, 3H), 5.10(s, 2H), 6.08(s, 1H), 7.00-7.95(m, 7H)

The other hand, the compound(II) used for preparing glyoxylate of the formula(IV) may be synthesized by the methods disclosed in M. Ranbaud, M. Bakasse, CT.

Duguay and J. Villieras, Synthesis, 564(1988). ; Org. Synth. Coll. Vol. 5, 329, and the compound(III) can be prepared by the methods disclosed in H. Dorn, Chem. Heterocycle. Compd. (Engl. Transl.), 16,1 (1980) ; A. R. Katritzky and F. W. Maine, Tetrahedron, 20, 315(1964).



(II)



(III) (IV)

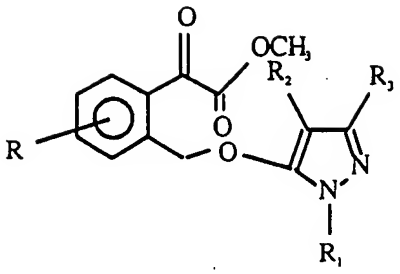
In the above reaction scheme, organic solvent such as chlorobenzene, tetrahydrofuran, dimethylformamide, etc. may be used to convert the compound of formula(II) into the formula(IV). The completion of reaction for obtaining the compound of formula(IV) is when no more the compound of formula(II) is remained. It can be easily checked by T.L.C or G.C.

The compound of formula(II) which is the starting compound from this step may be used in molar equivalent with compound(III) and potassium carbonate and sodium hydride of 1 ~ 3 equivalents may be used respectively.

When the reaction is completed, the product is washed with water and the used solvent was evaporated. The desired compound(IV) can be obtained by chromatography, and its structure was conformed by NMR, MS, etc.

Novel glyoxylate derivatives of the following formula(IV-a) and (IV-b) as obtained from the above manufacturing process are typically listed as the following Table 3 and 4.

Table 3.

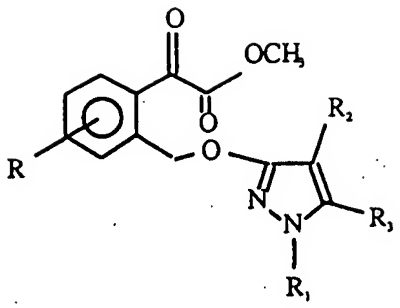


(IV - a)

Comp. No.	R	R_1	R_2	R_3
70	H	CH_3	H	CF_3
71	H	CH_3	H	Cl
72	H	CH_3	H	CHF_2
73	H	CH_3	H	H
74	H	CH_3	H	CH_3
75	H	CH_3	Br	CH_3
76	H	CH_3	Cl	CH_3
77	H	CH_3	CO_2Et	H
78	H	C_2H_5	H	CF_3
79	H	i-Pr	H	CF_3
80	H	c-Pr	H	CF_3
81	H	CH_2CF_3	H	CF_3
82	H	$CH_2CH=CH_2$	H	CF_3
83	H	$CH_2CH\equiv CH$	H	CF_3
84	H	n-Bu	H	CF_3
85	H	i-Bu	H	CF_3
86	H	phenyl	H	CF_3
87	H	2-pyridyl	H	CF_3

Comp. No.	R	R_1	R_2	R_3
88	H	3-fluorophenyl	H	CF_3
89	H	3-chlorophenyl	H	CF_3
90	4-Cl	CH_3	H	CF_3
91	4-Cl	C_2H_5	H	CF_3
92	3-Cl	CH_3	H	CF_3
93	3,4-Cl_2	CH_3	H	CF_3
94	3-NO_2	CH_3	H	CF_3
95	3-CH_3	CH_3	H	CF_3
96	4-CH_3	CH_3	H	CF_3
97	3-CH_3O	CH_3	H	CF_3
98	4-CH_3O	CH_3	H	CF_3
99	4-C_2H_5	CH_3	H	CF_3
100	4,5 	CH_3	H	CF_3

Table 4.



(IV - b)

Comp. No.	R	R_1	R_2	R_3
101	H	CH_3	H	CF_3
102	H	CH_3	H	Cl
103	H	CH_3	H	CH_3
104	H	CH_3	H	H
105	H	CH_3	H	CF_3
106	H	C_2H_5	H	CF_3
107	H	i-Pr	H	CF_3
108	H	c-Pr	H	CF_3
109	4-Cl	CH_3	H	CF_3
110	4-Cl	C_2H_5	H	CF_3
111	3-Cl	CH_3	H	CF_3
112	3,4-Cl_2	CH_3	H	CF_3
113	3-NO_2	CH_3	H	CF_3
114	4-NO_2	CH_3	H	CF_3
115	4-CH_3	CH_3	H	CF_3
116	4-CH_3O	CH_3	H	CF_3
117	4-C_2H_5	CH_3	H	CF_3
118	4,5 	CH_3	H	CF_3

EXAMPLE 18 (Typical Synthesis of compounds in Table 3)

Methyl-2-[2-(1-methyl-3-trifluoromethyl-5-pyrazoyl)-methyl-phenyl]glyoxylate (Comp. No. 70)

To a solution of 2-methyloxalylbenzyl bromide(1.7g, 6.65 mmole) in dimethyl formamide(15*ml*) at room temperature was added 1-methyl-3-trifluoromethyl-5-hydroxypyrazole (1.16g, 7 mmole) and potassium carbonate (1.2g, 8.6 mmol). The reaction mixture was stirred at room temperature for 12hr, and then quenched by addition of diethyl ether(70*ml*) and water(40*ml*). The queous layer was extracted with diethyl ether. The combined organic extracts were washed with water, dried over anydrous magnesium sulfate, filtered, and concentrated undder reduced pressure to crude product. Final purification was effected by silica-gel column chromatography (ethyl acetate-hexane 1 : 3) to afford the compound No. 70(1.4g, yield=70%).

^{1}H NMR($CDCl_3$): δ 3.80(s, 3H), 4.00(s, 3H), 5.75(s, 2H), 5.95(s, 1H), 7.50-8.00(m, 4H)

m/e : 342(M^+)

EXAMPLE 19 (Typical synthesis of compounds in Table 4)

Methyl-2-[2-(1-methyl-5-trifluoromethyl-3-pyrazoyl)-methyl-phenyl]glyoxylate (Comp. No. 101)

To a solution of 2-methyloxalylbenzyl bromide(1g, 3.9mmole) in dimethylformamide(10*ml*) at room temperature was added 1-methyl-5-trifluoromethyl-3-hydroxypyrazole(690 mg, 4.1mmole) and potassium carbonate (710mg, 5.1mmol). The reaction mixture was stirred at room temperature for 12hr, and then quenched by addition of diethyl ether(50*ml*) and water(30*ml*). The aqueous layer was extracted with diethyl ether. The combined organic extracts were washed with water, dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure to crude product. Final purification was effected by silica-gel column chromatography(ethyl acetate-hexane, 1 : 3) to afford the compound No. 101 (900mg, yield=68%).

^{1}H NMR($CDCl_3$): δ 3.85(s, 3H), 3.89(s, 3H), 5.56(s, 2H), 6.10(s, 1H), 7.06-7.97(m, 4H)

m/e : 342(M^+)

The present invention is directed to the fungicidal compositions comprising the fungicidal compound of the present invention as an active compound. Said fungicidal compositions can be formulated in various forms, such as aqueous dispersions, emulsions, dusts, granules and so forth. These compositions are preferred to comprise one or more active compounds of the present invention with one or more suitable adjuvants such as carriers and diluents which are chemically inert to the active compound.

The exact concentration of the active compound in a composition thereof with an adjuvant therefor can vary ; it is only necessary that the active compounds be present in sufficient amounts so as to make possible the application of a fungicidally effective dosage.

For example, in the case that the compositions are emulsions or aqueous dispersions, the amount of the active compound is preferred to range from 10 to 90% by weight.

And in the case of dust compositions, said amount is preferred to range from 0.1 to 30% by weight, also in the case of granule compositions, the amount is preferred to range from 1 to 30% by weight. But, the amount of the active compound in the compositions is somewhat variable according to the purposed use of the compositions.

Preferred carriers which are employed in the compositions according to the present invention are liquid carriers which are selected from alcohols(i.e. monohydric alcohols like methanol, dihydric alcohols like ethyleneglycol, and trihydric alcohols like glycerine, etc.), ketones(i.e. acetone, methylethylketone, etc), ethers(i.e. dioxane, tetrahydrofuran, cellosolve, etc.), aliphatic hydrocarbons(i.e. gasoline, kerossene, etc.), hydrocarbon halides(i.e. chloroform, carbon tetrachloride, etc.), acid amides(i.e. dimethylformamide, etc.), esters(i.e. butyl acetate, ethyl acetate, glyceride, etc.), and nitriles(i.e. acetonitrile, etc.), and solid carriers which are selected from mineral

compounds such as kaoline, clay, bentonite, acid clay, talc, diatomaceous earth, silica and sand, and vegetable powerds such as arbor. Above referred liquid carriers can be used separately or in company with one or more other liquid carriers.

The fungicidal composition of the present invention may include emulsifying agents, spreaders, dispersing agents or permeating agents. Also, the composition may include nonionic, anionic or cationic surfactants, for example, fatty acid soda or polyoxyalkylesters, alkylsulfonates or polyethyleneglycolethers.

On the other hand, one of the compounds of the present invention or compositions containing the same, can be advantageously employed in combination with one or more additional known pesticidal compounds which are active agricultural chemicals. Such additional pesticidal compounds may be insecticides, herbicides, plant hormones and sterilizers, and if necessary, fertilizers.

Composition 1 (Emulsion)

Compound No. 1-1	20%	(by weight)
xylene	75%	
polyoxyethylen glycolether	5%	

The foregoing components were mixed to form an emulsion composition.

Composition 2 (Dusts)

Compound No. 1- 2	5%	(by weight)
kaoline	94.6%	
silicon (antifoaming agent)	0.3%	
polyoxyethylen glycolether	0.1%	

The foregoing components were mixed to form a dust composition.

Composition 3 (Aqueous dispersion)

Compound No. 2-1	30%	(by weight)
sodium lignosulfonate	5%	

polyoxyethylene glycolether	5%
bentonite	60%

The foregoing components were mixed to form an aqueous dispersion composition.

Composition 4 (Granules)

Compound No. 2-2	10%	(by weight)
sodium lignosulfonate	5%	
bentonite	85%	

The foregoing components were kneaded using with water and formed into a granule composition.

The superior fungicidal activities of propenoic ester derivatives(I) according to the present invention prepared by the above examples were tested to check protective effect against the barley powdery mildew, the wheat leat rust, the rice blast and rice sheath blight. A 10% acetone solution containing the compound(I) was diluted using Tween-20 solution of 250 ppm strength(500 ppm in the case of rice). Five hundred *ml* of this chemical solution was sprayed to plants of equal height and allowed to stand at room temperature for 24 hours. After evaporation of spray solution and water, the test plants were inoculated with target fungi. The tests were carried out two times by the same method.

In the case of a fungicidal rate of 100%, the concentration of the test chemicals was gradually reduced until the EC_{50} value, namely the concentration(ppm) which gives an fungicidal rate of 50%, was determined.

TEST 1

Fungicidal Test for Rice Blast (RCB)

Pyricularia oryzae Cavara KJ301 as test rice blast fungus was selected and inoculated on rice polish agar medium(Rice polish 20g, Dextrose 10g, Agar 15g, D.W.

1hr) to incubate at 26℃ for 2 weeks, and then scratched airial mycelia with Rubber Polishman were irradiated with near fluorescent light to form spore at 25 ~ 28℃ for 48 hours.

A suspension of conidia in water(10^6 spores/*ml*) was prepared and sprayed upon the 3 ~4 leaf stage of rice plants on the foliage. After placing in dark dew chamber for 24hours, the treated plants were then held in lighted growth chamber(26 ± 2℃, 80%) for 5 days, and rated on the disease severity. The disease severity was examined against the percent disease area on the first leaf right under 3 ~ 4 leaf stage and compared to the standard rating diagram.

TEST 2

Fungicidal Test for Rice Sheath Blight (RSB)

Rhizoctonia solani AG-1 was incubated in wheat bran medium (1 *l* , bottle), and then the agar disc was inoculated in growth chamber(27 ± 1℃) for 7 days.

Rice plans in the 2 ~ 3 leaf stage in 5cm pots were inoculated with the milled conidia. After incubating in dew chamber(28 ± 1℃), the disease severity was examined against the percent disease area on the applied leaf of 2 ~ 3 leaf stage and compared to the standard rating diagram.

TEST 3

Fungicidal Test for Wheat Leaf Rust (WLR)

Test was made to succession culture of Puccinia recondita against the host plants. For the succession culture and the fungicidal effect tests, wheats(cultivar ; chokwang) were grown in polyvinyl pots(diameter ; 6.5cm) for 7 days, and then spores of the first leaf stage were inoculated.

After placing the treated wheat in dew chamber at 20℃ for 1 day, the plants was held in growth chamber(20℃, 70%) for 10 days, and then rated on the disease severity.

The disease severity was examined as the percent disease area after inoculating

the spores for 10 days.

TEST 4

Fungicidal Test for Barlley Powdery Mildew(BPM)

Tests were made to succession culture of Eysiphe graminis &. sp. hordei. For the succession culture and the fungicidal effect tests, barley(Dongbori No.1) was grown in polyvinyl pots(diameter ; 6.5cm) for 7 days, and then spores of the first leaf stage were inoculated.

The treated barley was held in growth chamber(22 ~ 24℃, 50%), and the disease severity was rated after 7 days inoculation.

In the above Test 1 ~ 4, those compound which produced an insecticidal rate of 100% at 500ppm and, for comparison, commercial fungicidals (controls) were tested according to the method mentioned above, and the EC_{50} values were determined. The results are shown in Table 5.

EC_{50} value means the concentration(ppm) which a fungicidal rate of 50%.

The fungicidal rate of the test chemicals was determined according to the following ;

$$\text{Control value}(\%) = \left(1 - \frac{\text{Percent of disease area in treatment}}{\text{Percent of disease area in untreated contral}}\right) \times 100$$

Table 5.

Comp. No.	RCB	RSB	WLR	BPM
1	125	100	< 2	2
2	25	25	10	< 2
3	-	97	25	5
8	-	-	50	50
14	112	96	50	5
15	120	115	25	50
21	-	-	10	5
22	-	-	10	10
31	-	40	25	25
44	120	90	< 2	< 2
45	25	10	< 0.4	< 0.08
58	70	5	7	3
Flusilazole	-	-	2	0.08
Fenarimol	-	-	2	0.08
Comp. A*	< 100	-	< 100	100
Comp. B**	-	-	160	50

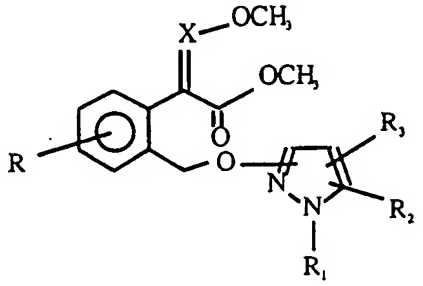
(Note)

* Comp. A : Propionic ester compound disclosed in European Patent No. 472300

** Comp. B : Propionic ester compound disclosed in European Patent No. 460575

WHAT IS CLAIMED IS :

1. Propenoic ester derivatives having pyrazole group of the following general formula(I) which have active fungicidal properties



(I)

wherein,

R is hydrogen, one or more halogen atoms selected from the group consisting of fluorine and chlorine, methyl, lower alkyl, alkoxy, nitro or phenyl group ;

R_1 is methyl, lower alkyl, alkenyl, alkynyl, benzyl, aryl, phenyl, substituted phenyl or pyridyl group ;

R_2 and R_3, as equivalent or different group respectively, are hydrogen, halogen atoms, trifluoromethyl or haloalkyl group ; and

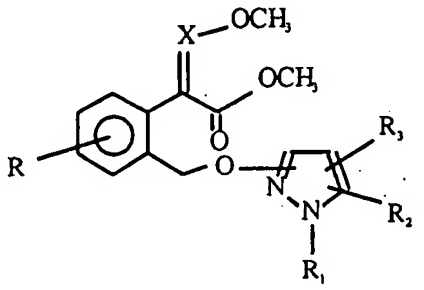
X is carbon or nitrogen atom.

2. Propenoic ester derivatives which correspond to the claim 1, wherein R is hydrogen or chlorine atom.

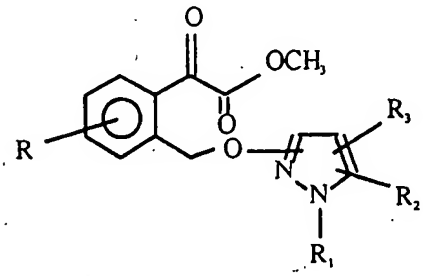
3. Propenoic ester derivatives which correspond to the claim 1 to 2, wherein R_1 is methyl or lower alkyl group.

4. Propenoic ester derivatives which correspond to the claim 1 to 3, wherein R_2 and R_3, as equivalent or different group respectively, are hydrogen atom or trifluoromethyl group.

5. Glyoxylate derivatives having the following general formula(IV), as an intermidate of propenoic ester derivatives of the following general formula(I) whic have active fungicidal properties



(I)



(IV)

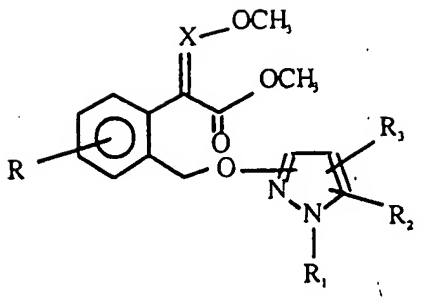
wherein, R, R_1, R_2, R_3 and X are respectively defined as the above claim 1.

6. Glyoxylate derivatives which correspond to the claim 5, wherein R is hydrogen or chlorine.

7. Glyoxylate derivatives which correspond to the claim 5 to 6 wherein R_1 is methyl or lower alkyl group.

8. Glyoxylate derivatives which correspond to the claim 5 to 7, wherein R_2 and R_3, as equivalent or different group respectively, are hydrogen atom or trifluoromethyl group.

9. A fungicidal composition containing active compound corresponding to propenoic ester derivative of the following general formula(I)



(I)

wherein, R, R_1, R_2, R_3 and X are respectively defined as the above claim 1.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR 93/00052

A. CLASSIFICATION OF SUBJECT MATTER

IPC[5]: C 07 D 231/12, 231/14; A 01 N 43/56

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC[5]: C 07 D 231/12, 231/14; A 01 N 43/56

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

DARC, CAS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE, A1, 3 905 948 (BASF AG) 30 August 1990 (30.08.90), claims 1-3.	1,5,9
A	EP, A2, 0 278 595 (IMPERIAL CHEMICAL INDUSTRIES PLC) 14 January 1988 (14.01.88), claims 1,7,12,23,24.	1,5,9
A	EP, A2, 0 350 691 (BASF AKTIENGESELLSCHAFT) 24 June 1989 (24.06.89), claims 1,2,3,4.	1,5,9

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 September 1993 (13.09.93)	22 September 1993 (22.09.93)

Name and mailing address of the ISA/ AT	Authorized officer
AUSTRIAN PATENT OFFICE Kohlmarkt 8-10 A-1014 Vienna	Brus e.h. Telephone No. 5337058/45

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
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